BNL-80221-2008-BC

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To be published in "Aberration Corrected Microscopy"

April 2008

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BNL-80221-2008-BC

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Table of contents

1. INTRODUCTION

The last decade witnessed the rapid development and implementation of aberration correction in electron optics, realizing a more-than-70-year-old dream of aberration-free electron microscopy with a spatial resolution below one angstrom [1-9]. With sophisticated aberration correctors, modern electron microscopes now can reveal *local* structural information unavailable with neutrons and x-rays, such as the *local* arrangement of atoms, order/disorder, electronic inhomogeneity, bonding states, spin configuration, quantum confinement, and symmetry breaking [10-17]. Aberration correction through multipole-based correctors, as well as the associated improved stability in accelerating voltage, lens supplies, and goniometers in electron microscopes now enables medium-voltage (200-300kV) microscopes to achieve image resolution at or below 0.1nm. Aberration correction not only improves the instrument's spatial resolution but, equally importantly, allows larger objective lens pole-piece gaps to be employed thus realizing the potential of the instrument as a nanoscale property-measurement tool. That is, while retaining high spatial resolution, we can use various sample stages to observe the materials' response under various temperature, electric- and magnetic- fields, and atmospheric environments. Such capabilities afford tremendous opportunities to tackle challenging science and technology issues in physics, chemistry, materials science, and biology.

The research goal of the electron microscopy group at the Dept. of Condensed Matter Physics and Materials Science and the Center for Functional Nanomaterials, as well as the Institute for Advanced Electron Microscopy, Brookhaven National Laboratory (BNL), is to elucidate the microscopic origin of the physical- and chemical- behavior of materials, and the role of individual, or groups of atoms, especially in their native functional environments. We plan to accomplish this by developing and implementing various quantitative electron microscopy techniques in strongly correlated electron systems and nanostructured materials. As a first step, with the support of Materials Science Division, Office of Basic Energy Science, US Department of Energy, and the New York State Office of Science, Technology, and Academic Research, recently we acquired three aberration-corrected electron microscopes from the three major microscope manufacturers, i.e., JEOL, Hitachi, and FEI. The Hitachi HD2700C is equipped with a probe corrector, the FEI Titan 80-300 has an imaging corrector, while the JEOL2200MCO has both. All the correctors are of the dual-hexapole type, designed and manufactured by CEOS GmbH based on the design due to Rose and Haider [3, 18]. All these three are one-of-a-kind in the US, designed for specialized capabilities in characterizing nanoscale structure. In this chapter, we review the performance of these state-of-the art instruments and the new challenges associated with the improved spatial resolution, including the environment requirements of the laboratory that hosts these instruments. Although each instrument we describe here has its own strengths and drawbacks, it is not our intention to rank them in terms of their performance, especially their spatial resolution in imaging.

2. ENVIRONMENTAL REQUIREMENTS AND LABORATORY DESIGN FOR ABERRATION-CORRECTED ELECTRON MICROSCOPES

An aberration-corrected electron microscope aims at a sub-angstrom spatial resolution, or an improvement to a fraction of an angstrom in performance. This is not a trivial task. Besides needing a skillful operator who can tune the corrector and optimize the electron-optics of the instrument, it is a prerequisite to house the instrument in an environmentally stable laboratory with a minimal amount of floor vibration, acoustic noise, air flow and fluctuation in air pressure, temperature, and interference from electromagnetic fields. Very often, environmental instabilities are the limiting factors in achieving the expected performance of an aberration-corrected electron microscope. Since images are acquired serially in STEM, any instabilities would appear as image

distortions, while in the parallel recording of HRTEM (e.g., through-focus series acquisition) would result in a loss of contrast and ultimately, of resolution. Indeed, an aberration corrector only corrects electro-optical aberration of the microscope, not any of the instabilities. The double-aberration corrected JEOL2200FS TEM/STEM located in the Department of Condensed Matter Physics and Materials Science (CMPMS), Bldg.480, at BNL services as a good example (Fig.1). Before installing this microscope, we designed a new laboratory, completely renovating a 50-year-old building previously used as a gym. The changes were based on the required specifications with < 0.5mG rms (root-mean-square, which equals one sixth of the peak-to-peak (p-p) measurement) electro-magnetic fields at 60Hz, a maximum airflow rate of 15ft/min, and a temperature stability of 0.1ºC/hr. Although active vibration-compensation systems were available, low frequency vibrations (10Hz and below) are best attenuated by large masses. To decouple the instrument from the vibrations emanating from surrounding laboratories, we cut the floor and poured a 2ft-thick concrete slab on which the instrument sits, isolated with de-coupling materials at the slab's perimeter. To ensure the low airflow rate without jeopardizing the required temperature stability, we chose, as an air-supply inlet, a U-shaped tube covered with a small-pored "duct sox" that minimizes air movement. Since the electromagnetic field throughout the laboratory was on the borderline of the requirement ranging from 0.2 to 0.5mGauss, we installed an electromagnetic field-cancellation system (see Fig.1) to test the effectiveness of the system in compensating for potential changes in the background AC and DC fields. The compensation system did not work as well as expected, which we largely attribute to the small compensation we were seeking, and because such a system can only cancel the field at one point in the room or on the microscope.

Electromagnetic interference and stray magnetic fields, especially at the level above 0.5mG, can induce considerable aberrations in HRTEM and scanning distortions in STEM imaging and EELS. Initially, we encountered a problem of STEM image distortion [19] due to 60Hz noise that was associated with a ground-loop in close proximity to the instrument (both in single- and three-phase circuits, the AC field generated by the grounding is inversely proportional to the grounding resistance, or proportional to the current lost to ground). After we eliminated the main source of the 60Hz noise, the quality of the STEM images were greatly improved.

The BNL JEM2200FS was equipped with an in-column energy filter that is better electro-magnetically shielded compared to the post-column energy filter. The "clamshell" for the sample stage recently designed and provided by JEOL helps to reduce the fluctuation of air pressure. Nevertheless, the design of the instrument was largely based on the JEM2010F and JEM2010FEF with a small 25cm-diameter column. Our study suggests that the aberration-corrected JEM2200FS is more susceptible to airflow and electromagnetic fields than a conventional (i.e., uncorrected) JEOL instrument such as JEM2010F, which demonstrated an achievable STEM atomic resolution with airflow as high as 15ft/min [20]. Significantly lower airflow rates are required for the JEM2200FS due to its much longer column. Since the stiffness of a microscope's column improves roughly with the 4^{th} power of its diameter but deteriorates by the 3^{rd} power of its length, increasing the length by adding correctors and energy filters therefore might dramatically lower the instrument's performance.

Recognizing the importance of the laboratory environment on the performance of the high-resolution instruments [21], we expended considerable effort on designing and constructing the electron-microscopy suite at the Center for Functional Nanomaterials (CFN, building 735, completed in May 2007, HDR Architecture, Inc), one of the five nanocenters in the DOE's nationwide complex. The CFN site was carefully selected within BNL's 5300 acre site for its few sources of vibration and electromagnetic interference. The entire building was constructed on

compacted structural fill that was compressed to 98% maximum dry density using various vibration methods.

The electron-microscopy suite, located on the ground floor of the building, consists of six microscope laboratories and one sample preparation laboratory. Four microscope rooms originally were designed as high-accuracy laboratories for aberration-corrected microscopes, each consisting of an Instrument Room, an Equipment Room and a Control Room (Fig.2); only two were constructed due to their unexpectedly high cost. The design criteria for the high-accuracy laboratories include floor vibrations below 0.25μm/sec (rms) in all directions and frequencies, acoustic noise below 40dB, stray AC magnetic fields < 0.1mG (p-p) at 60Hz and at lower frequencies scaled by f/60, stray DC field below 1mG vertical, below 0.01mG horizontal above earth ambient field, airflow <1cm/min vertically, and no horizontal air current permitted. Temperature and humidity were set at 21.1±0.1ºC/hr (70±0.18ºF/hr) and 40-60%, respectively.

The facility is located in the south side of the building, far away from vibrations induced by street traffic and from the elevator on the north side of the building. All the laboratories are adjacent to a 3m (10ft) Galley that houses all vibrating equipment, such as vacuum pumps and water chillers. We placed additional shielding along the wall to limit magnetic emanations from the Galley. Compared to the building slabs that are 15 cm (6 inches thick) (4 kips/in^2), the floor slabs under the high-accuracy laboratories are 60 cm (24 inches) thick, reinforced with number five reinforcing bars every 30 cm (12 inches) top and bottom, and are isolated with a half-inch isolation joint between the building columns and other slabs. The slab for the Control Room also is 60cm (24 inches) thick and separated with a half-inch isolation joint. Furthermore, the top six inches of the slab contain a vibration-reducing agent “Concredamp” that is reinforced with polypropylene fibers, which also was placed in the Galley spaces.

The Instrument Room (Fig.3), ~3.7m(W)×5.3m(D)×4.6m(H) (12ft×17.5ft×15ft), of the high-accuracy laboratory was constructed with a room-in-room concept. An equipment area (Equipment Room, ~2.6m×5.3m×4.6m (8.5ft×17.5ft×15ft)) was built outside the inner room (Fig.2). We adopted this design for two reasons. The first was to minimize the heat load in the Instrument Room, so that a minimum amount of cooling would be needed there. The second was that the microscope’s power supplies added possible fluctuations in the noise- and heat-loads. Moving them to the space between the inner and outer rooms ensured that they were in a well-controlled environment but outside the most sensitive instrument area. A 15cm (6") space between the 3 inner and outer walls serves as a return air plenum. The walls and outer ceiling are constructed from prefabricated modular panels consisting of 100% 10cm (4" thick) polyurethane foam insulation bonded by an adhesive to an aluminum outer skin. The inside of the Instrument Room offers a superb acoustically insulated wall surface, and a support for the radiant wall panels. The Equipment Room also was constructed from prefabricated panels with gasketed, insulated doors, similar to freezers with good sealing. Double-glass panels, ~6.8mx2.6m (22.5ftx8.5ft), between the Instrument Room and the Control Room (Fig.4) allow the operator to see inside the Instrument Room. Double doors with a total opening of 1.5m by 2.4m (5ft by 8ft) provide access to the Instrument Room. Although we laid down isolated slabs for the four high-precision laboratories, only two, 1L30 and 1L24, were finished with the original room-in-room design; they currently house the Hitachi and FEI aberration-corrected microscopes, respectively. The other two laboratories will be developed and expanded in future. Fig.5 shows the vibration measurement on one of the slabs in the microscope laboratory. We did not detect vibrations or an acoustic noise peak at 30Hz (often associated with the ventilating motors and pumps running at 1800rpm) in the Instrument Room, and very little 4-10Hz frequencies associated with belt-driven equipment.

The Equipment Rooms (Fig.2) are air conditioned through a constant volume VAV box from 100% outside air using an air handler. Silencers installed in the air handlers reduce acoustic noise. All air handlers in the building are direct-drive units specified for low vibration and noise. The air pressure in the Equipment Rooms is slightly positive at 2.5 pa (0.010 in. w.c.) to keep dust out. The Instrument Rooms originally were meant to use laminar-flow air for 6 m/min (20 fpm) maximum. Later, we modified the design, and placed radiant cooling panels (approx 30 Btu/sqft of panel area) in the ceiling and walls, thereby attaining almost zero airflow in the room. Currently, to assure adequate ventilation for operators, we exhaust only 4.6 m/min (50 cfm) from the room through an exhaust grill located at floor level, the rate can be increased up to 27.9 m/min (300 cfm) during maintenance. Air-flow measurements show 0 m/min horizontally in the space, and typically 0 to 0.3m/min (1 FPM) vertically. In a normal day (a 24hr period) without people in and out of the Instrument Room, a temperature fluctuation below 0.017ºC (0.03ºF) can be achieved (see Fig.6).

The radiant cooling system is isolated from the site's 5.5ºC (42ºF) water with a heat exchanger, and the water temperature is held at 12.2ºC (54ºF). Piping was sized to keep the flow velocity below 0.9m/sec (3FPS), and panels were sized at 0.6m/sec (2 FPS) to reduce noise. The variable speed drives on the radiant cooling loops allow us to adjust flows to more closely match the system's characteristics to actual cooling loads in the rooms. The aluminum acoustic ceiling panels used as radiant panels both on the walls and the ceiling reduce noise in the room. The perforation sizes in the ceiling panels are just big enough to distribute the required airflow for cooling at reasonable velocities. Smaller holes in the panels increase their acoustic attenuation. In addition, we placed acoustic blankets enclosed in plastic above the microscope's column to blank off air flow over the column and provide additional sound attenuation. Temperature sensors (thermistors) at multiple locations (Fig.3) with high-resolution transmitters constantly monitor the temperature of the Instrument Room and the entire system is remotely computer- controlled.

The room's humidity is maintained between 30 to 50% Rh. The makeup air into the space is cooled to 10ºC (50ºF) for dehumidification, while a humidifier is available should we need to increase humidity. We planned for the possible formation of condensation on the cooling panels by installing a humidity-sensor system to calculate dew point temperature. The controller resets the radiant cooling-water temperature upwards if the difference between the water's temperature and room's dew point is less than 1.1ºC (2ºF).

The microscope laboratories have both fluorescent- and incandescent-lighting. The former is used for maintenance, while the incandescent fixtures are dimmable, eliminating the radio-frequency interference that is generated from the solid-state electronic ballast of the fluorescent fixtures. The floor tiles are conductive and grounded to eliminate electrostatic charges. The area in the microscope suites and adjacent laboratories is considered a high-sensitivity area, and accordingly, all circuits there above 120 VAC are enclosed in rigid metal conduits and all conductors are twisted to mitigate the magnetic fields generated from the power circuits. The microscope equipment has a special dedicated equipment ground. All local electrical panels and transformers serving the high-accuracy rooms have aluminum and steel shielding to reduce electrical noise. Furthermore, the building's main switchgear electrical room is totally shielded in two layers. The outer layer is a 6mm (1/4") thick aluminum plate with welded seams, while the inner layer has two layers 6mm&3mm (1/4" & 1/8") of low- carbon steel plates to give a total plate thickness of 9mm (3/8 inch). The major feeder runs to the upstairs mechanical room are shielded to reduce stray magnetic fields that would impact the high-accuracy laboratories.

The distribution transformers feeding the panels were isolated to establish a "clean" transformer for laboratories and sensitive equipment, and a normal panel feeding non-sensitive equipment.

Normal lighting and building equipment are fed from the "non-sensitive" distribution panels. The microscope's manufacturer added an uninterrupted power supply (UPS) for more isolation, filtering, and safe orderly shutdown of the microscope and its subsystems. Electrical trenches within the floor slab accommodate the cabling from the microscope equipment, thereby eliminate the hazards of having them running across the floor.

Both Hitachi and FEI room surveys before their instrument delivery showed very low magnetic fields in the high-accuracy labs. In general, in all x, y, and z directions at different heights in the Instrument room, the measured AC fields are below 0.005mG. Figure 7 shows the measurement of the Hitachi laboratory (IL30) in May 2007 when the building was just completed without any scientific equipment moved in. Our own measurements in early 2008 using the Spicer Consulting Analysis System (SC11) suggest the average AC magnetic fields at 60Hz of the room IL30 after the instrument is in operational are about 0.15mG in z-direction and 0.08mG in x-y directions. An interesting observation is the dissimilar acoustic spectra measured in rooms 1L24 and 1L30 that were designed identically. The only difference between them when the measurement was taken was the presence of the operational STEM in 1L30 (room 1L24 was in its as-built state). We recorded a source of acoustic noise from the mechanical fan used to cool the scan coils that were not in the lens water-cooling system. It increases the noise level from 38 to 44dB.

3. THE BNL ABERRATION-CORRECTED INSTRUMENTS

3.1. The JEOL JEM2200FS and JEM2200MCO TEM/STEM

The Brookhaven JEM2200MCO TEM/STEM (see Fig. 8) is based on JEM2200FEF TEM/STEM that features an in-column Omega-type energy-filter. The instrument consists of a probe corrector for STEM and an imaging corrector for TEM as well as a double-Wein-filter monochromater [22]. We placed the purchase order in early 2002. When this chapter was written, the monochromater had gone through several iterations of redesign, and had not passed its required specifications at the factory. The prototype version of the instrument, JEM2200FS (Fig.1), which has a probe corrector, was loaned to BNL before the final instrument (JEM2200MCO, MCO refers to monochromated, aberration-corrected and omega filtered instrument) could be built. The JEM2200FS was installed at BNL in December 2004 and the JEM2200CMO in October 2006 in the JEM2200FS room after the loaner instrument was sent from BNL to University of Illinois at Urbana Champaign. The monochromator is scheduled for delivery to BNL and retrofitting to the JEM2200MCO in the fall of 2008. Recent test results with the monochromator at the factory showed an energy resolution of 0.18eV with a beam current of 10pA at a probe size of 2nm. The target for the probe size in STEM for the instrument is 0.07nm. The performance details of the BNL JEM2200FS were reported previously [19, 23].

The Brookhaven JEM2200MCO microscope is a sister instrument to the one installed at Oxford University, UK, also in Oct. 2006 (the performance of the Oxford loaner instrument JEM2200FS can be found in [9]). Besides the Omega filter and two aberration correctors, it has a 200kV thermo-assisted Schottky field-emission electron gun, an ultra-high-resolution pole-piece (URP) with a ±25° sample tilt, and a Gatan GAT894 2kx2k Ultrascan CCD camera (active area 28.7mmx28.7mm). Instead of using a fluorescent screen it has a Hamamastu camera. It is also equipped with a JEOL STEM BF and DF detector and a Faraday cup. The JEM2200CMO has several important improvements over the JEM2200FS. Since it has to accommodate two aberration correctors and a monochromator the total column height of the instrument can reach over 4m (the measured height of BNL's microscope is 3.68m without the monochromator compared 2.5m height for JEM2100F). To support the relatively tall and thin column, a large

rigid metal frame was added to the instrument (Fig.8). Nevertheless, the new instrument still seems susceptible to perturbations in airflow. Fig.9 shows the quality of the STEM image resolution under various conditions of airflow. Figs.9(a-b) show before and after the air-duct near the column was covered with aluminum foils, while Fig.9(c) shows the effects of an additional heavy curtain half-way down below the sample stage, and, (d) with the air-conditioner off. Differences in the image distortion are clearly visible. Power-spectrum analysis of Young's fringes of Au particles in TEM mode (Figs.9(e-h)) indicates that there was a directional reduction of frequencies transmitted, or attainable resolution, in the case of Fig.9(e) and (f), while there are no remarkable differences in Fig.9(g) and (h).

The JEM2200MCO also has electro-optical design improvements, with an additional intermediate lens, an additional projector lens and a piezo-controlled stage in all x, y, z directions. The ability to use the piezo control to adjust the focus, or z-height of the sample, without change of the objective lens current is particularly convenient for corrector alignment. The stability of the high tension of the instrument was improved from $1.0x10^{-6}$ to $3x10^{-7}$and the lens current stability was improved from 1ppm to 0.5ppm, compared with the JEM2200FS.

The geometrical aberrations of the objective lens and probe-forming lens in the instrument can be corrected up to third order. The aberration correctors can be tuned either manually or using CEOS' auto-alignment software [24]. After properly tuning the corrector, either in TEM, or STEM, the aberration coefficients A2 and B2 are typically smaller than 150nm, and S3, A3, and C3 are smaller than 5μm. On-site acceptable tests demonstrated in both aberration-corrected TEM and STEM imaging a 0.1nm point-to-point resolution in Fourier space. Measurement of a STEM image of a silicon single-crystal in [110] orientation shows that a dip contrast at or better than 20% between the adjacent dumbbells can be achieved (Fig.3.3a). The power-spectra of the images show the (400) and the (511) diffraction spots, indicating the limit for attainable information is beyond 0.1nm (Fig.10b). The Ronchigram analysis in STEM mode suggests that the constant phase area is extended from 14mrad before aberration correction to nearly 35mrad afterwards (Fig.11). This means that instead of using a 15mrad convergence-angle for an uncorrected STEM, we can routinely employ a 30mrad convergence-angle, which allows a three-fold increase in probe current. In STEM, the maximum probe current is 100pA with the probe corrector off at beam size of 0.5nm.

JEOL's in-column filter is advantageous for quantitative electron diffraction by filtering unwanted electrons, especially in convergent-beam electron diffraction. The filter's acceptance angle is about 60mrad for a 4eV slit, and 170mrad with no slit (Fig.12). The isochromaticity of the omega filter is about 2eV with an area of view of the full 2kx2k CCD camera. The filter also can serve as an electron energy-loss spectrometer (EELS), in particular for spectroscopy imaging. However, for most spectroscopic applications, it has an intrinsic drawback because it lacks an aberration-correction system to minimize the spectra distortion. Consequently, to curtail distortion the smallest entrance aperture must be used for EELS, thus significantly reducing the flexibility of choosing different collection angles and beam intensities. Furthermore, the energy resolution for the Omega system typically is 1.0-1.1eV for the normal emission current (~100uA), and about 0.7eV for low emission current (~30uA).

Fig.13(a) shows an example of HREM imaging of a 3° tilt grain boundary in $SrTiO_3$ bi-crystal using JEM2200MCO. Compared with conventional HREM images from an uncorrected microscope, there is notable increase in image contrast due to the reduction of the contrast delocalization effects. Furthermore, corrections were made for the presence of the three-fold aberration, so that the images are better suited for quantitative analysis [19]. Fig.13(b) and (c), respectively, are a reconstructed rotation map and a strain map from the same image in Fig.3.6(a)

using Geometric phase analysis [25, 26]. The color scheme shows the ±1.5° rotation of each grain and a 15% expansion and compression of the lattice near the dislocation cores.

3.2 The Hitachi 2700C STEM

The BNL Hitachi HD2700C is located in the newly established Center for Functional Nanomaterials (CFN). It is the first aberration-corrected electron microscope manufactured by Hitachi. The instrument is based on HD2300 [27], a dedicated STEM developed a few years ago as an alternative for the discontinued VG STEMs. The BNL instrument has a cold-field-emission electron source with high brightness and small energy spread, ideal for atomically resolved STEM imaging and EELS. The microscope has two condenser lenses and an objective lens with a 3.8mm gap, compared to the 5mm-gap objective lens in HD2300, with the same ±30º sample tilt capability and various holders for heating and cooling (-170~1000°C). The projector system consists of two lenses that provide considerable flexibility in choosing various camera lengths and collection angles for imaging and spectroscopy. Table I summarizes the convergent angles and collection angles for various settings. There are seven fixed and retractable detectors in the microscope. Above the objective lens is the secondary electron detector for imaging the sample's surface morphology. Below are the Hitachi analog HAADF and BF detector for STEM, and a Sony TV rate (30frame/sec) 8bit CCD camera (480×480) for fast and low magnification observations and alignment. The Gatan 2.6k×2.6k 14 bit CCD camera located further down is for diffraction (both convergent and parallel illumination) and Ronchigram analysis. The Gatan analog MAADF detector and EELS spectrometer (a 16bit 100×1340 pixel CCD) are sited at the bottom of the instrument. The spectrometer (Enfina ER) is a high-vacuum compatible high-resolution device that Gatan designed particularly for BNL. The CEOS probe corrector, located between the condenser lens and the objective lens, has 2 hexapoles and 5 electromagnetic round lenses, 7 dipoles for alignment, and 1 quadrupole and 1 hexapole for astigmatism correction. Other features of the instrument include remote operation, double shielding of the high-tension tank and anti-vibration system for the field emission tank. The entire instrument is covered with a telephone-booth-like metal box (Fig.3) to reduce acoustic noise and thermal drift. The instrument was installed in July, 2007. Within the first two weeks, we had achieved a 0.1nm resolution of the HAADF-STEM image [28]. The instrument was accepted in November 2007. We recently added a residual gas analyzer (RGA-200, Stanford Research Systems) to monitor vacuum quality, especially relative to specimen contamination.

Figure 14 shows an HAADF STEM image of $BaTiO_3$ recorded with an inner collection angle of 53mrad. The contrast between Ba and the background is 56%. Since the HD-2700C is equipped with a high-dynamic-range Gatan CCD camera, this dedicated STEM allows us to record CBED (Fig.14c, Silicon (100) with convergence angle of 1.7mrad and probe size smaller than 10nm) and nanobeam diffraction (Fig.14d, Silicon (100) acquired with 28mrad convergence angle). Fig.14e shows a Ronchigram of this microscope with a half angle of flat region of 43mrad with the aberration corrector on. In addition to preset modes, the microscope can operate in a variety of combinations of convergence angles and collection angles by using free lens control. Regarding EELS capability, Fig.15 illustrates a time trace of the zero-loss peak of the 200kV electron beam during 130 sec; it indicates a stability of less than $8x10^{-7}$ for this duration. The energy resolution derived from this experiment is 0.35eV (FWHM) for a 10sec acquisition.

Single heavy atoms on a thin (<4nm) carbon film represent a simple specimen from both a practical preparation and an analysis point of view. We selected uranium atoms for high Z, easy availability and characteristic core-loss spectrum for atomic EELS and STEM (Fig.16). The sample is typical of negative staining employed in biological studies except that the uranyl acetate

is 100x more dilute. Tobacco mosaic virus (TMV) was included to give a thickness gradient with higher concentration of uranium atoms near the TMV, sometimes forming small clumps. The UO_2 species observed on such a specimen has a nearest neighbor spacing of 0.34nm, but the atom size "seen" by the electrons scattered onto the dark field annular detectors is much smaller.

Figures 17 are sequential images excerpted from a movie of uranium single atom motion. Single atoms move due to irradiation by the electron beam. During this experiment the specimen was cooled to -160º C with a Gatan 670 liquid nitrogen cooling stage [29]. In an electron microscope, the detection of a single atom is accompanied by the passage of a high-energy electron within 0.5Å of the atom [4, 5]. Therefore, there is a significant probability that the atom will gain enough energy to remove it from its binding site; hence, a sequence of images will contain information about the movement of individual atoms, limited only by the time resolution of the image acquisition. This behavior is determined by the balance of several bonding energies, including Van der Waals forces, molecular orbital- and bonding-valence electrons state, surface energy, and electric attraction and repulsion. However, enough atoms remain stationary on sequential scan lines and from frame to frame to permit reliable measurement of probe diameter.

3.3 The FEI Titan 80-300 ETEM

The FEI Titan 80-300 is an instrument newly designed to fully realize the benefits of aberration correction in TEM/STEM. The Titan's large column diameter (30cm), compared with the JEOL2200MCO, 25cm, and the Hitachi HD2700C 24cm, was specifically designed for mechanical- and thermal-stability with the added length of the probe and image correctors and monochromator. The column assembly also is of the modular type wherein each module/lens section can be aligned accurately, and the aberration correctors and monochromator can be retrofitted with relative ease. The instrument sits on three active vibration dampers to further reduce mechanical vibration. Its unique design of proprietary constant power lenses and power supplies provide the needed thermal- and electronic-stability.

The BNL FEI is an 80kV to 300kV TEM/STEM with a thermo-assisted Schottky field-emission electron gun (Fig.18a). The advantages of higher acceleration voltages are both improved spatial resolution and increased current in a small probe. The acceleration voltage of the instrument can be switched between 80-300kV. The low-kV setting is particularly attractive for radiation-sensitive materials, such as graphene and carbon nanotubes, since it is below the knock-on damage threshold of carbon, as well as for EELS with its slightly improved energy resolution. The challenge is then to scale performance in line with the theoretical performance reduction due to the longer wavelength.

The microscope, also located in the new CFN building, is a versatile instrument, with its SuperTWIN objective lens and a CEOS imaging-corrector mounted between the objective lens and the first intermediate lens (or diffraction lens) for HREM. It has a scanning unit with a Fischione HAADF detector for atomic-resolution STEM. Its other components include: a Lorentz lens (built into the CEOS corrector) for magnetic imaging and a bi-prism for electron holography, an EDAX energy dispersive x-ray system (EDS), a Gatan 2kx2k top camera, and 863 Tridiam spectrometer (2kx2k CCD) at the bottom. The large pole-piece gap (5.4mm) of the objective lens and the five-axis motor-driven CompuStage support a ±40º tilt of the sample. The instrument also has several sample holders for heating, cooling, and tomography capabilities, and various software for data acquisition and analysis, including HREM through-focus reconstruction, low-dose exposure, dynamic conical-dark-field and tomography reconstruction.

The illumination system of the microscope comprises three condenser lenses. Together, they form a double-zoom system (Koehler illumination) giving increased flexibility in both the TEM and STEM mode. In the former mode, parallel illumination can be achieved over a wide field of view. In the latter, a large variety in probe angles and probe currents is available.

The instrument has two intermediate lenses and a projector lens for diffraction and imaging at different camera lengths and magnifications. The Lorentz lens is a separate small lens that is located at the bottom of the objective-lens' lower pole piece (quite similar to the mini-condenser lens, but with the main difference that it has a separate water-cooling circuit). The Lorentz lens occupies an intermediate position between objective lens on and off. Typically attainable maximum magnification values for the Lorentz lens are ~60kx as opposed to ~3kx for the low magnification mode, and the resolution lies between 1.5-2nm.

Configuration of the BNL instrument was finalized in late 2005. The main feature was its environmental cell or E-cell. FEI has built E-cells in the past, for the CM300 at Haldor Topsøe in Demark, in 1999, and for the Tecnai F20 at Arizona State University in 2002; nevertheless, BNL was the first to request FEI for an aberration-corrected E-TEM to study chemical reactions and catalysis. The E-cell has a gas-inlet system with 4 inlets connected to the objective-lens' octagon. A needle valve that can regulate gas flows in small steps is sited at the gas-inlet system so to maintain a stable pressure in the E-cell. The special vacuum system enables researchers to observe a specimen under a gas pressure up to 20mbar, while maintaining a workable high vacuum in the rest of the TEM column and field-emission gun. Various gases can be utilized, such as He, N_2, CO_2 and H_2O, but some gases must be handled with utmost care because of fire- or explosion-hazards (e.g., CH_4, H_2), toxic properties (e.g., CO), or strong contamination effects (e.g., sulfur-based gases). The instrument is equipped with a residual gas analyzer (PGA Pfeiffer Prisma QMS 200).

The E-TEMs that FEI previously built had a vacuum around 10^{-5} torr in the sample area. Nevertheless, we realize that imaging and spectroscopy quality, especially in STEM mode, is sensitive to vacuum quality. This is particularly important for E-TEM, where a clean environment at the sample before any reaction has taken place is crucial for interpretation of experiment data. Particular attention was paid to the *in situ* vacuum system of BNL's E-TEM. There are 5 Ion Getter Pumps (2 for the gun, 2 for the column, and 1 for the E-cell), 5 Turbo Molecular Pumps (1 for the column and sample air- lock, 1 for the projector chamber, and 3 for the E-cell), along with 2 Scroll Pumps as backup. In the *in-situ* mode, the ion Getter Pump (IGP) is switched off and the valve towards this IGP is closed. Other valves are open to allow pumping of the column by the *in-situ* system. Gas is introduced to the E-cell via another valve. A BaroCell measures the gas pressure. Two fixed differential pumping apertures inside the tip of the upper- and lower-objective lens pole- pieces restrict the gas flow from the E-cell into the rest of the column. Special pumping measures were taken to evacuate a large portion of this gas flow via the *in-situ* tubing. To obtain the required pressure ratio, some additional bypasses were implemented in the column of the TEM allowing a change in the vacuum level of 10 orders-of-magnitude within a distance less than 0.5m between the E-cell and the FEG's emission chamber.

Even though the E-TEM system entails significant modifications to the microscope, the system still will support normal TEM operation, and its resolution and performance is uncompromised compared to a standard Super-TWIN system. Although the system is not yet suited to reach the true UHV pressure levels, in high-vacuum mode, attainable pressure is $5x10^{-6}$ Pa. The main limitation is the lack of differential pumping in the moving bearings, or O-rings, of the sample stage, or goniometer. Based on our agreement with FEI, if the piezo-controlled stage that does not use O-rings materializes (currently under development within the US DOE TEAM project),

then FEI will make the stage available for us, and thus, we will be able to significantly improve the vacuum of the system.

When the system has been running in the ETEM mode (with gas) after switching to standard mode, often the vacuum quality is too low to allow high-resolution STEM. This problem reflects strong sample contamination or etching. We unsuccessfully requested a sample pretreatment chamber and a heating lamp in the sample loading dock. With the help of FEI, a de-contaminator, or RF plasma-cleaning system (model Evactron 45, manufactured by XEI Scientific, Inc.) has been installed at the octagon of the objective lens, or E-cell (Fig.18b). The RF plasma ignites and produces oxygen radicals that clean the sample and the chamber. The source of the oxygen radicals is a down-flowing remote plasma device that does not directly expose the chamber or sample to plasma. The general underlying principle is that the plasma generates active species that flow into the chamber and react with the contaminants to produce volatile compounds that are removed by the vacuum pumps.

Special care must be taken in gas-reaction experiments. For example, electrons scattered by gas atoms reduce image contrast, increase background noise, and hasten the aging of the detector. IR radiation of the heating holders also increases the background signal. It is a good practice to retract the EDS detector when in E-TEM mode, or when the specimen is heated, using EELS for compositional analysis in the E-TEM mode. The beam's opening angle and field of view at the specimen is limited because of the differential pumping apertures in the objective lens pole pieces, as is the maximum detector angle in STEM mode.

The Brookhaven FEI E-TEM was installed in October 2007. One week after the start of the installation, the instrument in TEM mode showed an information limit of 0.7Å using Young's fringes of Au particles, demonstrating the stability of the instrument. Fig.19 shows the information limit test at different operation modes with E-cell's 3 Turbo Pumps Running mode without gas (Fig.19(a)) and with gas (Fig.19(b)), both operated at 300kV. Fig.19 (c) shows the E-cell 3 Turbo Pumps Off mode without gas at 80kV. The instrument can achieve energy resolution of 0.66eV and 0.54eV at 300kV and 80kV, respectively (Fig.20) at low-emission (extraction voltage at 3000V, compared to the normal operation condition of 4000V for TEM and 4500V for STEM). Fig.21 shows an image of twinning of a Au particle taken at 300kV right after the E-cell test with the Turbo pumps running. A 211 Silicon dumbbell image with a separation of 0.78A is shown in Fig.22 with a contrast dip of about 20%, using the through focus series and exit wave reconstruction method.

4. A BRIEF COMPARISON OF THE THREE INSTRUMENTS

Each of the three aberration-corrected electron microscopes at Brookhaven has its own strengths and weakness. Although all are capable of atomic imaging and spectroscopy, there are subtle differences in their electro-optics design to accommodate other capabilities. They are sufficiently different to preclude comparisons. Table II is a summary of the major features of the three instruments. Since they all have STEM capabilities that are very sensitive to the instrument's stabilities, we briefly discuss their performance within this context.

All three aberration-corrected instruments have a 1Å specification on STEM imaging resolution. They all achieve visible separation of Si 110 dumbbell images with a contrast dip, defined as $(I_{max}-I_{dip})/(I_{max}+I_{min})$, of 25% and better. All the three manufacturers used the high-order diffraction spot (say 511) of the FFT from Si dumbbell images to signify an achievement of 1Å and beyond in spatial resolution. In fact, this is not a convincing method since an instrument's

spatial resolution is defined by its ability to separate two objects in real space. The intensity or visibility of high-order reflections in FFT depends on many factors, including the test samples, not only on the spatial resolution of the instrument.

The STEM operation of the Hitachi HD2700C is probably the "simplest" since it is a dedicated STEM and does not have other accessories to interfere with the STEM operation and performance. The cold FEG of Hitachi is extremely beneficial as it offers high brightness and a small energy spread. Compared with a monochromator, it has much higher beam current and is much easier to use, and can reach an energy resolution at 0.35eV under normal operation conditions. The Hitachi instrument appears to give consistently reasonable STEM image resolution showing separation of Si 110 dumbbells at any given time. The aberration corrector improves the beam current by a factor of 10; our test results reveal that this probe current is about 200pA at 0.14nm probe size, and 400pA at 0.2nm.

The JEM2200CMO STEM also demonstrated well separated Si 110 dumbbells (Fig.10), although most times we see scanning distortion, which can likely be attributed to the imperfection of the laboratory environment. Nevertheless, with the aberration corrector on, the specification on probe current, 50pA at 0.15nm, still was not demonstrated when this chapter was written (March 2008). The energy resolution of the instrument during operation is about 1eV at normal emission current. The unique advantage of the JEM2200CMO is its in-column omega filter that is invaluable for quantitative electron diffraction. However, this advantage becomes a significant drawback in EELS performance since the filter does not have multilpole-lenses to correct its second order aberration of the omega filter, as does Gatan's post-column filter. For most EELS applications, the smallest entrance aperture must be employed to minimize the aberration and distortion in spectroscopy and spectroscopy imaging. With such an energy filter used as a spectrometer, the value of the monochromator for the instrument in EELS is increasingly questionable.

Amongst the three, the FEI 80-300 ETEM probably shows the best instrumental stability due to its large column diameter. An information limit around 0.07-0.08nm is routinely achievable using gold particles on carbon films in the TEM mode. Good Si 110 dumbbell STEM images without image distortion (90º lattice planes in images) have been frequently recorded (Fig.23). The energy resolution of the instrument using Gatan 863 Tridiem spectrometer seems better than the JEM2200CMO under normal operational conditions (probably by 10-15%). Since it does not have a probe corrector, comparison on beam current was not made.

A major issue we observe in the aberration-corrected STEM is the contrast reversal in annular dark-field (ADF) Z-contrast imaging. Because the condenser aperture can be opened up for a large convergent angle without inducing spherical aberration, the ratio of the convergence and collection angles falls sharply. Consequently, an ADF image is often not a true amplitude image anymore, but is mixed with phase information. Our recent study on thermalelectric $Ca_3Co_4O_9$, which has a layered structure of CoO_2 and Ca_2CoO_3 with a distinct difference in Co atomic density in adjacent atomic columns, revealed that when the ratio between the collection angles and the convergent angle is smaller than 3, contrast reversal might occur. Hence, care must be taken in interpreting the "Z-contrast" images. Details on contrast reversal in STEM ADF imaging will be reported elsewhere.

5. EVALUATION AND APPLICATIONS OF STEM

5.1 Overview

The challenge in STEM performance is simultaneous acquisition of atomically resolved ADF imaging and EELS. Since spectroscopy imaging necessitates a lengthy acquisition period (a 100x100 pixel map requires 10^4 times longer acquisition compared to a point acquisition), the quality of the data largely depends on the stability of the instrument that may be perturbed by various factors, including mechanical vibration, electrical noise, electromagnetic field, thermal drift, fluctuations in lens and emission current, and specimen charging. For each category, a monitoring protocol has to be established to detect any deterioration in performance, trace it to its source, and then correct it, otherwise the instrument will not perform as expected.

For any experiments involving small probes and long dwell-times, contamination of the specimens is a severe issue and is more acute for high-end instruments due to their high beam current and better detection ability. Contamination not only reduces considerably the signal/noise ratio but also makes interpreting quantitative data difficult; indeed, in the environment TEM (E-TEM), it can obscure in-situ chemical reactions. To minimize contamination, we have eliminated the use of oil-based diffusion pumps for all our microscopes. We have developed an analytical method to quantify the rate of contamination, and installed a gas analyzer to determine the source and ingredients. Generally, the problem is lessened by resorting to extended (overnight) pumping, pre-irradiation of a large area before data acquisition, or cooling (down to –160°C, which prevents surface migration and build-up of the contaminants). Extended pumping or pre-irradiation times are undesirable because they limit productivity. The unique plasma-cleaning apparatus for treating the sample inside our FEI microscope and various protocols we developed to maintain cleanliness, including transferring the sample from the cleaning chamber to the instrument, will help to circumvent the contamination problem.

A major emphasis of the BNL effort is development of imaging methods to permit *quantitative* comparison to theory as compared to "pretty pictures" with qualitative interpretation. Most commercial instruments automatically adjust contrast and brightness for optimum viewing (qualitative images), rather treating the signals as quantitative data (numbers), thereby often leading to misinterpretation. We have developed a routine to retrieve the absolute values of all detector signals to eliminate any ambiguity in interpretation. Furthermore, we develop and utilize image simulation software to predict image signals (in % of incident electron counts) for simple, well-characterized specimens and then collect data in various instruments for comparison as well as exploit our own cross-correlation algorithms to correct for sample drift. The effects of the delocalization of inelastic scattering have also to be addressed to retrieve the true structural information from 2D chemical images.

As we refine relevant parameters, we plan to move to more complex known cases and eventually to unknowns where we hope to be able to interpret images by quantitative comparison to models with a high degree of confidence. There is a general assumption that spherical aberration correction removes all artifacts and makes image interpretation foolproof. Our efforts to date show that this is not the case. Aberration-corrected instruments are usually operated at the largest aperture angle to maximize resolution. This has several side effects: 1) chromatic aberration increases in proportion to aperture size, 2) depth of focus also decreases proportionately, 3) coherent effects such as channeling become even more important, 4) more of the elastically scattered electrons remain within the cone of the incident beam, and 5) higher dose rate may accelerate specimen damage.

The effects of chromatic aberration and depth of focus are shown in Fig. 24. For reference, the diffraction-limited probe size decreases to below 1Å at 15 mrad, as shown. For a cold field emission gun with 0.25 eV energy spread and lens + corrector chromatic aberration coefficient of

0.7mm, the chromatic spread does not become an issue until the aperture reaches 40 mrad, whereas for a Schottky gun with 0.6 eV spread and no monochrometer, it can be a serious limitation at 25 mrad.

For an amorphous specimen, the depth of focus is only about 2nm. At that point the blurring becomes equal to the diffraction-limited probe diameter, increasing the effective probe size by a factor of 1.4 (effects added in quadrature). This is the basis of the depth sectioning, as described by Pennycook [8]. An obvious example of this effect is seen in viewing Ronchigrams during alignment of the aberration corrector. Theoretically the pattern should be flat and featureless when the probe is exactly focused on the specimen. In practice, that only happens when using specimens thinner than 2nm due to the fact that Ronchigrams from all specimen planes are mixed coherently in the final pattern (see Fig. 25).

In a crystalline specimen the defocus effect may be overcome by channeling, permitting atomic resolution on much thicker specimens. However, one needs to be aware that the beam amplitude trajectory within the specimen is *NOT* a simple transit down an atom column and minor imperfections (or thermal vibrations) can have significant ramifications. In order to understand this we have adopted a two-pronged approach: start with the simplest possible specimens and use quantitative image simulation to bootstrap to increasing levels of complexity. With image simulation, the intensity distribution at any plane within the specimen can be calculated.

5.2 Measurement of Probe Profile Using Single Atoms

Uranium atom images [29, 30] show clear bright spots with high signal-to-noise ratio and quantized intensity (Fig.16 and 17). Roughly 2/3 of atoms move less than 2Å on subsequent scans and have symmetrical profiles suitable for probe profile measurement. Occasionally a spot will have a flat side or a gap, indicating that the atom moved between successive scan lines. Uranyl ions have a tendency to form chains or clumps with 3.4Å spacing as well as vertical stacks that look like single atoms but with higher signal values. In the clumps, the atoms appear to stack nearly on top of each other so the substrate signal level is visible between bright columns and profile measurements of columns give nearly the same FWHM as single atoms.

From a practical point of view, use of this specimen as a "delta function" to measure beam profile is sensitive to contamination and atom motion. Atom motion falls into two domains: large jumps with unpredictable frequency and small movements due to thermal vibration. The large jumps are infrequent enough that many atoms can be traced from scan to scan and measured (both intensity and profile). Contamination can be eliminated by baking the specimen in the column overnight at 100°C and pre-irradiating a large area to polymerize the contaminant molecules. Alternatively, one can cool the specimen below -40°C to stop surface migration. Cooling could also help with atom motion, but it appears that the gross motion is beam-induced and not sensitive to temperature.

Figure 26 shows the simulated probe profile for a uranium atom on a 40Å thick amorphous carbon substrate as would be measured with various detectors. For comparison we include a scan over a point atom that gives the beam profile. Several points are worth noting: 1) the increase in full width half maximum (FWHM) due to the finite size of the atom is minimal, 2) the signal on the large angle (LA, 60-200 mrad) detector is roughly 3x less than on the small angle (SA, 30-60mrad), 3) a small shoulder on the probe profile is less pronounced on the detector signals and 4) the contribution of the substrate is essentially negligible. Assuming the effective diameter of the atom adds to the probe profile in quadrature, the effective atom size would be 0.20Å as seen by the SA detector and 0.1Å as seen by the LA detector. Therefore a specimen consisting of single

heavy atoms on thin carbon should be a good test of STEM performance. Figures 26 and 27 illustrate tests performed with the Hitachi HD2700C.

A similar specimen could be made using gold atoms and we find that the gold-island specimen used to align the corrector has numerous single gold atoms between large clumps. Uranium has the advantage of higher atomic number, giving 1.2x higher peak signal and a distinctive energy loss peak at 100 eV, which is suitable for EELS and chemical identification. Gold atoms do not have similarly distinctive spectrum. Also, gold atoms in clumps tend to stack in an fcc pattern with atoms over gaps in the lower layer, so atom columns are less evident in clumps.

5.3 Image Simulation

Image simulation provides a convenient way to sort out the importance of various factors in image formation. In a practical instrument the factors are usually interrelated in a complex way that makes it difficult to understand their individual importance. With simulations, one can use the same sample in a variety of circumstances. Our long-term goal is to develop quantitative imaging to the point where simulations agree with images within a few percent and significant differences indicate that the physics of the specimen is not what is being postulated.

The software package provided by Kirkland [31] is particularly useful in that it provides absolute intensities (100% of incident electrons are accounted for at the detector or image plane) in both TEM and STEM. We have added our own computer codes and software to generate atom coordinates of up to 10^7 atoms (floating point coordinates) in a single “unit cell” so both crystalline and amorphous specimens can be treated in the same way. We developed a subroutine to generate “amorphous” films having specified nearest-neighbor spacing. We also added display and linkage subroutines to expedite studies of imaging and nano diffraction in various scenarios. The Kirkland subroutines provide wave-optical propagation through optical elements and multi-slice coherent propagation through the specimen using parameterized atomic scattering factors.

There is an additional contribution to apparent spot diameter due to thermal vibration of the atoms. This is documented for many crystals but is only a guess for atoms free to move on a surface. Using the crystal value for silicon of 0.075Å, we expect the thermal contribution to be not measurable when added in quadrature. This is calculated by the "frozen phonon" method where atoms are given random displacements with RMS equal to the expected value and the results for roughly 10 runs averaged. In this case the expected probe diameter would increase from 0.473 Å to 0.479Å.

5.4 Quantification in Imaging and EELS

As described earlier, our long-term goal is to develop quantitative imaging. We have developed a procedure to calibrate the detector signals in terms of percent scattering. This involves reducing the annular detector gain by a factor of 10 or 100, removing the phase contrast aperture ahead of the bright field detector, positioning the direct beam (out of its normal position in annular detector hole) fully onto the annular detector and recording the signal relative to the bright field signal obtained with the beam aligned in the detector hole. We then restore the detector gain to high sensitivity, realign the beam and record AD and BF signals simultaneously during scanning. The normalization is done off-line on the recorded data. At each step care is taken to ensure that signals are never greater than 1/2 the saturation value of the recording system.

With single atom specimens on a thin amorphous substrate the signals are linear. The simulation software allows us to ask what happens as we stack up atoms or pack atoms into a crystal. The

small size of the probe suggests that an atom might block the beam from reaching atoms at lower levels. The actual situation is much more complicated due to the coherence of the beam, giving constructive and destructive interference effects. This is taken into account in the multi-slice calculation. In the case of stacked uranium atoms, the linearity breaks down after only a few atoms. However, thermal motions disrupt the exact alignment of the columns, giving nearly linear signal versus column height up to 4 atoms. A slight tilt of the specimen has the same effect.

A diffraction detector located in the detector plane permits direct visualization of the intensity of the scattered wave-front. The various annular and solid detectors integrate over portions of the pattern to give fast-response signals suitable for STEM imaging but discard much valuable information. Image simulation provides a convenient means to assess the information contained in the detector plane. Ideally we would like to record the entire pattern at each scanned pixel and dynamically configure a set of virtual detectors to extract the maximum amount of information. In the extreme case, we would use an algorithm to reconstruct the phases at each point in the detector plane (lost when the electron amplitude is converted to intensity by the detector). With the amplitude (square root of intensity) and computed phase, we could transform back to retrieve the exit wave at the bottom of the specimen. This form of "diffraction imaging" is being pursued by several groups in addition to our own (see 5.5).

Presently available detectors are not fast enough to record such a 4-D data cube, but there is rapid progress in that direction. However, we use the diffraction detector to view the Ronchigram to check the performance of the aberration corrector. In addition, the central portion of the unscattered disk gives a phase contrast image similar to that observed in TEM. Usually this is detected in STEM imaging by placing a small (3 mrad) aperture ahead of the bright field detector. This is comparable to TEM phase contrast with a 3 mrad illumination. Viewing the entire beam disc gives an in-line hologram. The region around the central disc gives a convergent beam electron diffraction (CBED) pattern. Both these are characteristic of the very local area probed by the beam so they can be used for nano-diffraction studies of defects, grain boundaries, etc. Modern STEM instruments have several intermediate condenser and projector lenses, as well as apertures of different sizes which can be chosen to give a diffraction limited probe size commensurate with illumination angle and a wide range of camera lengths that can be optimized for any nano-diffraction experiment (see Table I).

Complementary to the diffraction is electron energy loss spectroscopy (EELS). Both rely on keeping the beam stationary with respect to the specimen to within a small fraction of a beam diameter. For diffraction, that can be a matter of a fraction of a second but for EELS it can be many minutes. Aberration correction places proportionately greater demands on specimen drift, scan noise & drift, high voltage and lens current stability. In addition, the larger illumination angle requires a correspondingly larger entrance aperture to collect most of the energy loss electrons. If the specimen is more than a few atomic layers in thickness, careful attention must be given to depth of focus and channeling. The ability to obtain an image showing atom columns does not guarantee that the beam intensity is probing a single atom column all the way through the specimen. This question can be addressed by simulation and comparison to standard specimens of known structure. There is also the possibility that an atom column that is "invisible" in the dark field image (due to low atomic number) could still give an EELS signal.

From a practical point of view, a parallel EELS system (best for large entrance aperture) is relatively slow for spectrum imaging compared to a simpler system with a slit, since a spectrum must be recorded at each scan point. However the results can be more accurate since the full spectrum is available for background subtraction.

Based on the considerations described above, we have designated several generic types of study to assess the importance of various features and the factors in deciding which instrument to use. 1) Isolated catalyst particles (core/shell) on thin substrate: crystal structure, size & shape distribution, surface and bulk composition, and tomography; 2) Interface between two crystal phases, sectioned perpendicular to interface: strain due to mismatch, impurities at interfaces; 3) Doped crystals, dopant concentration and segregation; and 4) Thin filaments, supported only at ends. In addition to the obvious criteria of resolution and stability, key factors in selecting an instrument for a specific application are: speed of searching, ease of tilt alignment, eucentricity of tilt stage, ease of selection of operating parameters and automatic documentation database. In addition, specimen contamination and means to minimize it may be critical to some experiments, as well as specimen exchange time before stable operation can be obtained. We are attempting to arrive at generalizations to assist in allocating projects to specific instruments.

5.5 Position-Sensitive Coherent Electron Diffraction

For many applications, a fraction of an Angstrom improvement in spatial resolution of an instrument is not critical. A real value of a TEM and STEM corrector seems to lie in the large pole-piece gap that facilitates various *in-situ* experiments, and greatly increases probe current to achieve column-by-column spectroscopy imaging. A promising and exciting application in aberration-corrected STEM is position-sensitive coherent electron diffraction (PSCED) [32], similar to the method that is recently commercialized by Gatan [33]. In conventional STEMs, analog image intensity is recorded by integrating signals due to electrons passing through each scanning point of the sample over large annular ranges. Whilst the interpretation of the incoherent angular-integrated images is straightforward, a wealth of structural information is discarded in this angular integration, including the electronic- and magnetic-signals from the specimen. In PSCED, an electron diffraction pattern is acquired for each scanning position, i.e., an intensity distribution as a function of q in reciprocal space is recorded. In other words, we acquire signals of an object in reciprocal space (u,v,w) as a function of each scanning point in real space (x,y,z). For a 32x32 area detector, this gives ~1000 times more structural information for each scanning point than with a conventional STEM. A 1k by 1k detector will generate 10^6 times more data points. The signals of each scanning point would come from three parts: 1) Attenuation of the direct transmitted beam; 2) diffracted beams or scattered electrons striking the detector off axis; and, 3) deflection of the incident beam off the optical axis due to magnetic or electrical potentials and fields in the specimen. All of these signals can be recorded digitally for quantitative analysis. In general, electrons scattered at small angles are sensitive to charge and spin, while those scattered at large angles are sensitive to phonons and atomic positions. The information is paramount in nanoscale structure characterization. A major challenge to this development is processing the large quantity of data generated for each scanning point, as well as the need for an ultra-fast detector suitable for PSCED.

A novel position-sensitive detector, based on high resistivity silicon Active Matrix Pixel Sensors (AMPS) was recently designed, manufactured, and tested for PSCED at BNL [34]. Unlike the conventional CCD cameras used in electron microscopes, which convert electrons to photons and then back to electrons, the AMPS uses a direct-exposure format, thus eliminating the need for a scintillator and other electron-photon coupling components in the detector; hence, this design significantly improves the quantum efficiency of detection. The solid-state detector also gives fast parallel read-out of the number of electrons striking each of the pixels in an area array. Our calculations and preliminary test results suggest that the detection speed for a 32x32 array is about 10,000 frames per second with detection quantum efficiency better than 99.9%. The electronics noise of the read out corresponds to only about two thousand electron hole pairs. Compared with the 60,000 electron hole pairs generated by a single 200kV incident electron in

the silicon of the detector, at the anticipated low count levels per pixel, the AMPS detector counts the true number of incident electrons in the STEM. With such a detector, not only have we the sensitivity to detect single electrons, but also can distinguish pixels with, say, 30 counts from those with 31 counts.

To interpret the wealth of new information that will emerge from position sensitive electron diffraction, we carried out simulations of such an experiment [32]. Fig.28(a) depicts the calculated convergent-beam electron diffraction patterns from an undecagold cluster (11 gold atoms) on a 2nm thick amorphous carbon substrate. The image is composed from 14x11 diffraction patterns (one corresponding to each scanning position). Four enlarged patterns are shown in Fig.28(b). We used a probe size of 0.15nm with an increment of 0.05nm was used. The black circle in each pattern represents the disk of the transmitted beam and the intensity within the disk was attenuated by a factor of 100 for better visibility. We note the drastic change in intensity of the diffuse scattering surrounding the center disks when the probe scans across the area at a pace less than the interatomic distance of the specimen. Fig.28(c) is a reconstructed image from the diffuse scattering of the aperiodic gold cluster on amorphous carbon, together with a structural model of the Au cluster on its right. The integrated intensity of the center disks also can be used to form a bright-field image that maps the mean inner potential of the scanned area. Simulations based on 10^6 or more atoms of specified atomic number and spatial coordinates can be used to evaluate feasibility of proposed experiments and optimum imaging conditions.

7. OUTLOOK

Aberration correction provides superior spatial resolution in microscopy and ample opportunities for materials research, however, it does not automatically make interpretation of experimental data easier. The real challenge in electron-beam based structural characterization is quantitative electron microscopy, which in our view is the future direction of the field. Electron microscopy was traditionally used to visualize microstructure to understand mechanical properties, with the advancement in instrumentation, electron microscopy now becomes an indispensable tool, not only for materials science and nanotechnology, but also for physics, in parallel with neutron and synchrotron x-ray, to understand electronic and magnetic structure in complex functional materials. Although quantitative data analysis and interpretation are still rare, with our continued efforts, we will be able to dispel the perception that electron microscopy is only for imaging, and we microscopists only take pictures.

As we adapt to the new capabilities at hand, we begin a new wish list. One key consideration is specimen preparation. As depth of focus decreases and resolution improves, we are increasingly concerned about the few layers of contaminant coating the top and bottom of the specimen. The AFM and STM communities have already faced this issue and moved to UHV systems with integrated specimen preparation hardware. A related issue is the need to examine specimens in more than one instrument to obtain complementary information. Exposure to air and poor load-lock vacuum limits this. We need a UHV transit system standard for all analytical instruments. Unfortunately for electron microscopy, that probably means stage designs not dependent on specimen rods.

Another area sure to develop rapidly is direct electron detectors with smart electronics in the detector chip. These could be configured to approximate the bandwidth of present detectors but with many additional channels giving relevant specimen parameters. Similar detectors for EELS could enable spectrum imaging at the same rate as normal STEM imaging. For EELS detector, the ability of simultaneous acquisition of zero-loss and core-loss spectra (with attenuation for

zero-loss) is desirable for fine-structure and chemical shift analysis. Faster and more sensitive electron detectors are urgently needed not only for real-time aberration corrector alignment but for in-situ experiments to observe structural dynamics and transient states in materials. With better detectors and more coherent beams, PSCED could become a reality, giving separate amplitude and phase maps in reciprocal space of the specimen for studies of electronic and magnetic properties at nanometer scale.

ACKNOWLEDGEMENTS

We would like to thank Nomura, H. Inada and G. Hom for installing and testing JEM2200CMO, Hitachi HD2700C, FEI Titan 80-300, respectively, at BNL. We also would like to thank C. Channing and O. Dyling for their useful discussions and contribution on Sec. 2 of this chapter, R.F. Klie and C. Johnson for testing the JEM2200FS and 2200MCO. Assistance from various people in recording the data used in figures, Nomura (Fig.9), H. Inada (Fig.16-17), Y.C. Wang and L. Fu (Fig.21-23), is acknowledged. The work at BNL was supported by the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy Science, under Contracts No. DE-AC02-98CH10886.

Table I : Various pre-sets for different collection angles in the Hitachi HD2700C.

	ADF collection angle β	
mode	Hitachi detector (mrad)	Gatan detector (mrad)
HAADF[1]*	114-608	46-104
MAADF[2]*	53-280	21-49
CL1	64-341	26-59
CL2	45-242	18-41
CL3	24-126	10-22
CL4	16-85	7-15

Note:
1: High-angle annular dark-field detector
2: Medium-angle annular dark-field detector
*: not compatible with spectrometer focus.

Table II : The main features of the three aberration corrected instruments at BNL.

	FEI Titan	Hitachi	JEOL 2200
High tension	80-300	120-200	80-200
Electron source	thermal FEG	cold FEG	thermal FEG
Operation mode	TEM/STEM	STEM	TEM/STEM
Corrector(s)	imaging	probe	probe & imaging
Spectrometer	Gatan Tridiem	Gatan Enfina	JEOL omega filter

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